



IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant : Masahiro HAMADA et al.

Serial No. : 10/530,981

Filed : April 11, 2005

For : PROCESS FOR THE PRODUCTION OF  
SULFOALKYL-CONTAINING POLYMERS

Examiner : Zimmer, Mark S.

Art Unit : 1712

Confirmation  
No. :

Customer No. :

Attorney

Docket No. : 576P072

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August 20, 2007  
Date

Sir:

DECLARATION UNDER 37 C.F.R. §1.132

I, Masahiro HAMADA, a citizen of Japan residing at 2-336, Kitabukuro-cho, Omiya-ku, Saitama-shi, Saitama 330-0835 Japan, hereby declare:

That I am currently a research scientist of Technology Development Group in the Functional Chemicals R&D

Laboratories of the Research & Development Group of NIPPON KAYAKU KABUSHIKI KAISHA, and have been in that position since 2004;

That I hold a Master of Integrated Biosciences Degree in 2001 from University of Tokyo;

That I have reviewed the above-referenced patent application as well as the Office Actions, and I am familiar with its prosecution and the cited reference; and

That the following experiments were conducted by me or under my supervision, in order to prepare sulfomethylated poly-ether sulfone by the following experiments according to (1) the thiourea method disclosed in cited reference WO 98/04598 (Kubota et al.)( for example, EXAMPLE 1 "Sulfonation of 4-Bromobutylstyrene Crosslinked Copolymer" of Kubota et al.), (2) the EtOCS<sub>2</sub>K method disclosed in Kubota et al. (for example, EXAMPLE 2 "Sulfonation of 4-Bromobutoxymethylstyrene Crosslinked Copolymer" of Kubota), and (3) the dimethyl sulfide method disclosed in Makromol. Chem., Rapid Commun. 1, 297-302(1980)(for example, line5 from the bottom to last line in Experiment Parts) which is descried in page 2, lines 18-22 of the present specification; Frank Doscher et al., and determine an ion-exchange capacity of the obtained products.

(I) Experiments and results:

(1) Synthesis of sulfomethylated polyether sulfone by the thiourea method disclosed in Kubota

(i) Synthesis

After substituting the air inside of a 500 ml 4-neck flask with a stirrer, a thermometer, a reflux condenser, and a desiccant tube (containing calcium chloride in it) by nitrogen gas, 10.72 g of chloro-methylated poly-ether sulfone which was synthesized by the method described in the present Example 2, 100 ml of dimethyl sulfoxide and 4.11 g of thiourea were put into the flask, and stirred at 70 degree Celsius for 4 hours.

After temperature in the reaction system became lower, reaction products were precipitated by adding dropwise the reactant solution into 500 ml of acetone, and the precipitate was separated by filtering. Separating process by washing the precipitate with acetone and filtering under reduced pressure was repeated, and then the obtained products were dried at 75 degree Celsius. The product yield was 19.2 g.

Thus obtained products were put into a 500 ml 4-neck flask with a stirrer, a thermometer, and a reflux condenser, and then 40 ml of hydrogen peroxide aqueous solution (34.5%) and 40 ml of water were added thereto, followed by stirring at 50 degrees Celsius for 2 hours. The reaction products were separated by filtration after temperature in the reaction system becomes lower. Washing it with water was repeated, and the obtained products was dried at 75 degrees Celsius. The yield of the products was 12.8 g.

(ii) Results

The products obtained in this experiment could not be identified by Nuclear Magnetic Resonance (NMR) determination because the chemical shifts of methylene part of 3.7 to 3.9 ppm found in sulfomethylated polyether sulfone, for example, sulfomethylated polyether sulfone synthesized by the present invention, could not be found in chart of NMR of the obtained products. The chemical shifts of methylene part of 3.85 shows that the methylene is bonded with sulfo group. The obtained products have the chemical shifts of methylene part of 4.60 ppm instead of 3.85 ppm. It seem that said chemical shifts 4.60 ppm is chemical shifts of methylene group bonded with isothiuronium salt, which would be formed in the obtained products. In addition, several other unidentified peaks were observed in the chart of NMR of the obtained products.

Further, we could not determine an ion-exchange capacity of the obtained products because an aqueous

solution to be titrated became clouded and solid compounds were precipitated in the solution while titration was carried out. It was thought that the polymer immersed in the solution was decomposed by an aqueous solution of potassium hydroxide for the titration.

(2) Synthesis of sulfomethylated polyether sulfone by the EtOCS<sub>2</sub>K method disclosed in Kubota

(i) Synthesis

Into a 500 ml 4-neck flask with a stirrer, 5.08 g of chloro-methylated poly-ether sulfone which was synthesized by the method described in the present Example 2, 40 ml of N,N-dimethyl folmamide and 3.11 g of O-ethyl potassium dithiocarbonate(EtOCS<sub>2</sub>K) were put, and stirred at room temperature for 1 hour.

After 1 hour passed, the whole reactant solution had high viscosity. After the reaction solution was diluted in 50 ml of N,N-dimethyl folmamide, reaction products were precipitated by adding dropwise the solution into 100 ml of water, and the precipitate was separated by filtering.

Thus precipitated products were put into a 300 ml 4-neck flask with a stirrer, a thermometer and a reflux condenser, and then 27.15 g of hydrogen peroxide solution (34.5%) and 40 ml of water were added thereto, followed by stirring at 50 degrees Celsius for 2 hours. The obtained products were separated by filtration after temperature in the reaction system becomes lower. Washing it with water was repeated, and the obtained polymer was dried at 75 degrees Celsius. The yield of the products was 5.21 g.

(ii) Results

We tried to dissolve the products obtained in this experiment in any one of N,N-dimethyl folmamide, chloroform and dimethyl sulfoxide for Nuclear Magnetic Resonance (NMR) determination. However, the products could not be dissolved by in any one of said solvents although said sulfomethylated

polyether sulfone obtained by converting chloro-methylene group to sulfo methylene group usually dissolves in said solvents. Accordingly, NMR determination could not be performed.

It seems that the chloromethyl group of the chloromethylated poly-ether sulfone having high reactivity caused cross-linking reaction to produce cross-linked poly-ether sulfone which was insoluble to said solvents, among the reaction of chloro-methylated poly-ether sulfone and  $\text{EtOCS}_2\text{K}$ .

In addition, the obtained polymer was immersed in 2 wt% diluted sulfonic acid over night, washed enough with ion-exchanged water, and then dried at 75 degrees Celsius to obtain the proton-exchanged resin. A certain amount of the resin was measured off and immersed in aqueous solution of 0.1N sodium hydroxide over night. After the resin was removed, remaining aqueous solution of sodium hydroxide was titrated with 0.1N HCl. The ion-exchange capacity (the equivalent weight of sulfonic acid group) of the obtained polymer was determined by the titer.

The measured ion-exchange capacity was 0.46 mmol/g (= meq/g) which is equal to 2200 g/mol as the equivalent weight of sulfonic acid group. The products obtained by the  $\text{EtOCS}_2\text{K}$  method disclosed in Kubota did not show sufficient ion-exchange ability.

(3) Synthesis of sulfomethylated polyether sulfone by the dimethyl sulfide method disclosed in said Makromol. Chem., Rapid Commun.

(i) Synthesis

Into a 500 ml 4-neck flask with a stirrer, 3.99 g of chloro-methylated poly-ether sulfone which was synthesized by the method described in the present Example 2, 60 ml of methanol and 20 ml of dimethyl sulfide were put, and stirred at room temperature for 95 hours to disperse the poly-ether sulfone and carried out the reaction.

After the reaction, the dispersed poly-ether sulfone was aggregated. The reaction products were separated by filtering and then washed with methanol to obtain 3.88 g of the product.

Thus obtained products were put into a 300 ml 4-neck flask with a stirrer, a thermometer, and a reflux condenser, and then 50 ml of saturated aqueous solution of sodium sulfite was added thereto, followed by stirring for 5 hours. The solution was heated, and kept at 80 degrees Celsius for 51 hours. After temperature in the reaction system become lower, polymer was precipitated by filtration. Washing it with water was repeated, and the obtained polymer was dried at 75 degrees Celsius. The product yield of the polymer was 3.88 g.

#### (ii) Results

We tried to dissolve the obtained products same as mentioned in (ii) of above (2) for Nuclear Magnetic Resonance (NMR) determination. However, the products could not be dissolved by in any one of said solvents mentioned in (ii) of above (2) same as the products obtained (i) of above (2). Accordingly, NMR determination could not be performed.

It seem that the chloromethyl group of the chloromethylated poly-ether sulfone having high reactivity caused cross-linking reaction to produce cross-linked poly-ether sulfone which was insoluble to said solvents same as mentioned in above (ii) of (2).

In a similar manner as described above, the ion-exchange capacity (the equivalent weight of sulfonic acid group) of the obtained polymer was determined. The measured ion-exchange capacity was 0.01 mmol/g (= meq/g) which is equal to 120000 g/mol as the equivalent weight of sulfonic acid group. The products obtained by the dimethyl sulfide method disclosed in said Makromol. Chem., Rapid Commun. scarcely have ion-exchange ability.

(III) Consideration:

As far as our experiments mentioned above, (1) the thiourea method disclosed in Kubota et al. could not convert chloromethylated poly-ether sulfone to sulfomethylated poly-ether sulfone having ion-exchange ability, (2) the EtOCS<sub>2</sub>K method disclosed in Kubota et al. could prepare sulfomethylated poly-ether sulfone having insufficient ion-exchange capacity of 0.46 mmol/g (2200 g/mol as the equivalent weight of sulfonic acid group), and (3) the dimethyl sulfide method disclosed in Makromol. Chem., Rapid Commun. could prepare sulfomethylated poly-ether sulfone having less ion-exchange capacity of 0.01 mmol/g (120000 g/mol as the equivalent weight of sulfonic acid group).

In case of the method of the present invention, the sulfomethylated poly-ether sulfone of the present Example 2 has an ion-exchange capacity of 1.29 mmol/g (770 g/mol as the equivalent weight of sulfonic acid group) (the present specification, page 19, line 11-13) and, therefore, an ion-exchange resin having sufficient ion-exchange capacity could be prepared.

The method of the present invention can sulfonate chloromethylated poly-ether sulfone sufficiently deep in polymer matrix to obtain sulfomethylated resin which has solubility and is superior to workability, despite chloromethylated poly-ether sulfone has so high cross-linking reactivity that sulfonation by conventional methods is difficult.

I further declare that all statements made herein of my own knowledge are true and that all statements made upon information and belief are believed to be true, and further that these statements are made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment or both under Section 101 of Title 18 of the United States Code and that such willful false statement may jeopardize the validity of the above identified application or any patent issuing thereon.

Masahiro Hamada

Masahiro HAMADA

August 20, 2007

Date